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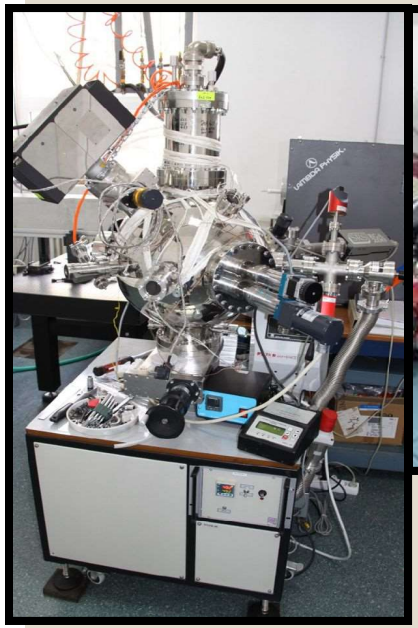
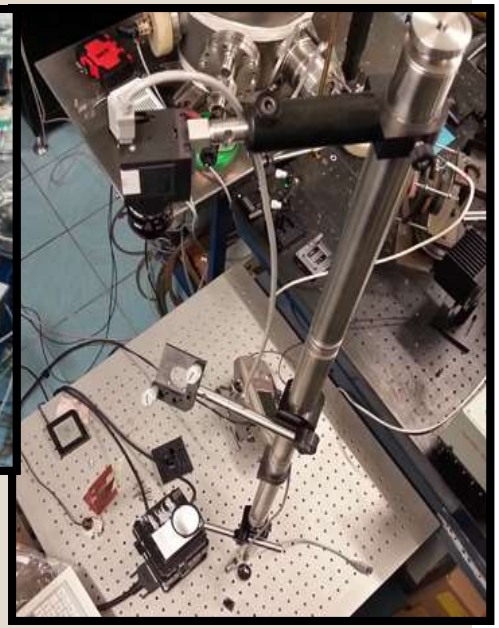
Material processing methods for sensor development



Pulsed laser deposition (PLD)

Matrix assisted pulsed laser evaporation (MAPLE)



Laser Induced Forward Transfer (LIFT)

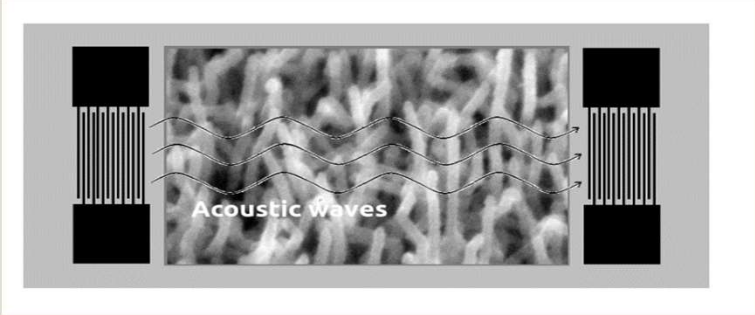
SENSORS

One of the most active research directions followed in the Lasers Department at INFLPR is the integration of new laser tailored materials for sensor applications.

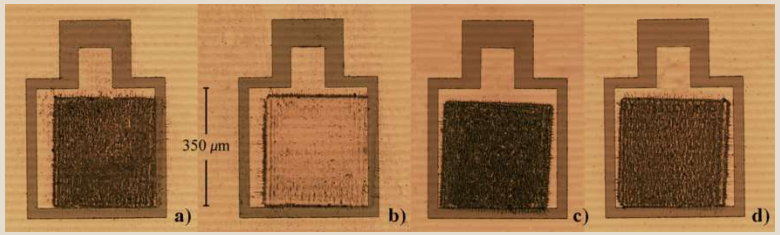
SENSORS

- Surface Acoustic Wave gas sensors:
  - Detection of chemical warfare agents (sarin, soman, cynahydric acid, lewisite, chloropicrin) at room temperature
  - Detection limit: low ppm range
  - Response time: few s
- Love-Wave sensors
- SAW sensors for hydrogen, hydrogen sulfide, and most common volatile organic compound detection at room temperature
  - Detection limit: low ppm range
  - Response time: below 10 s
- SAW biosensors for the detection of antigen-antibody response (detection limit 3 nM; possibility to analyze antigen-antibody reaction in real time) and odorant compounds found in the food industry (carvone and octenol).

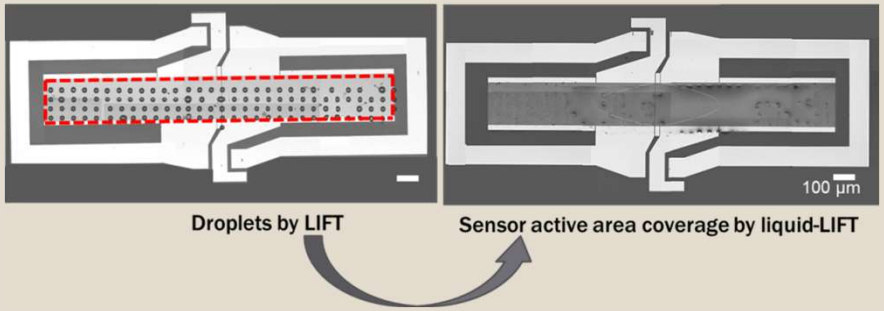
SAW



BAW

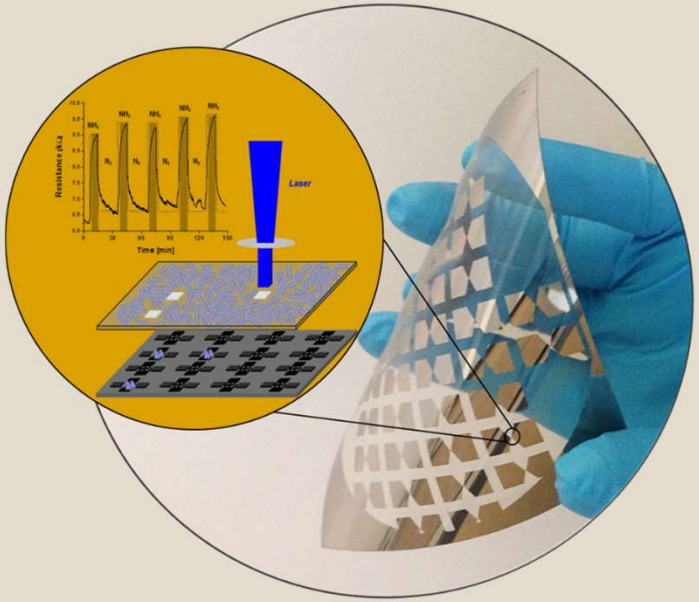


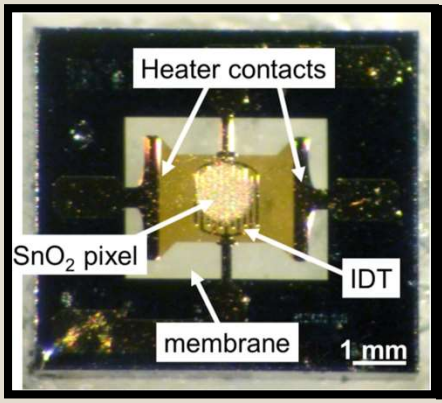
SAW - BIOSENSOR

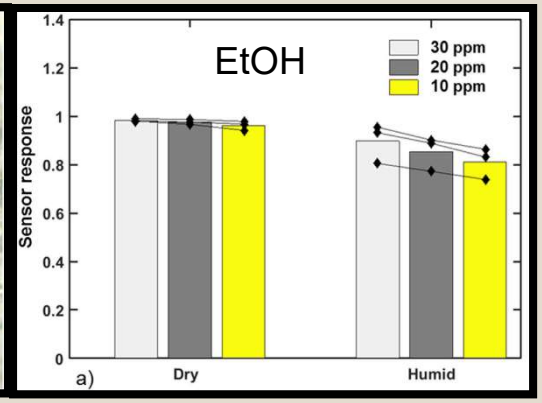


SENSORS

Chemiresistive sensors based on **carbon nanomaterials** (carbon nanotubes, graphene, carbon nanowalls) and **nanoparticles** (SnO_2, Pt, Pd, etc.)



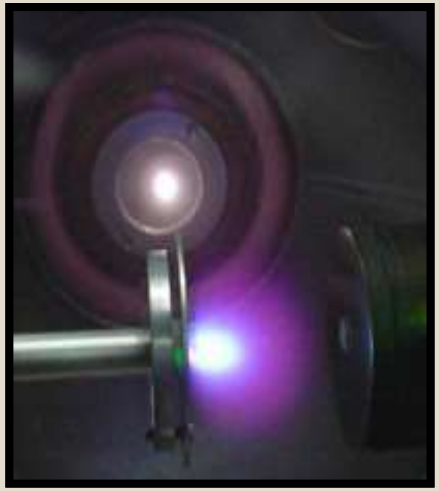


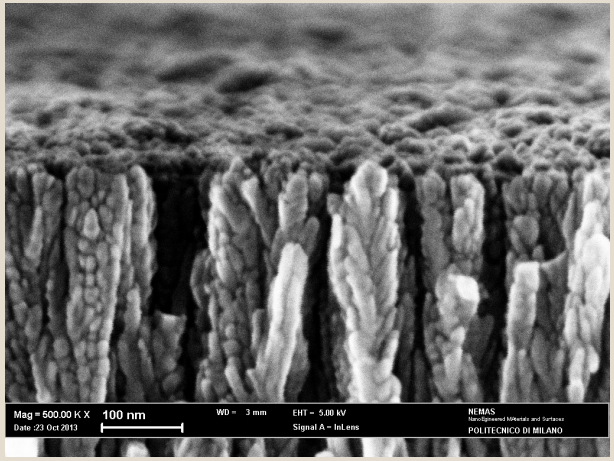


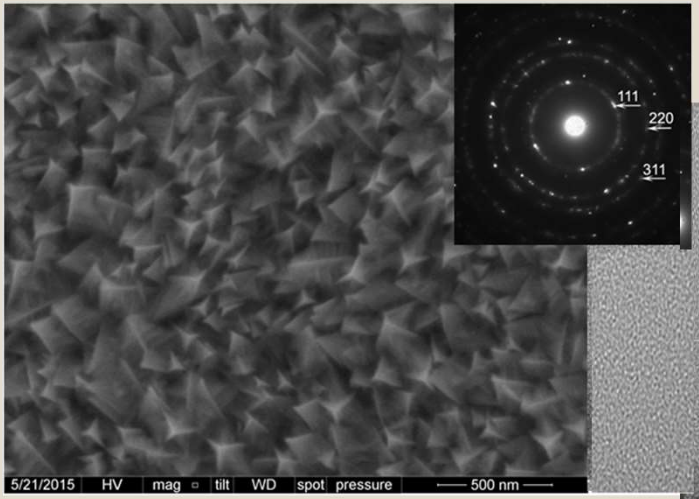
- Sensors fabricated by LIFT – possibility to fabricate sensors on **flexible substrates, roll-to-roll printing.**
- Mainly used for the detection of ammonia, ethanol (breath analyzer), methane, etc.
- Theoretical detection limits in the low ppb-ppt range, response time few s, stability over time.

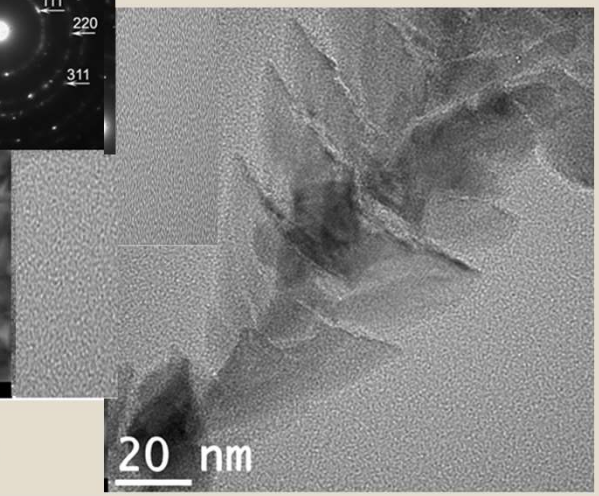
MATERIAL PROCESSING BY PLD AND RF-PLD

WO_3 nanostructured thin films obtained by the PLD for catalytic and sensor applications





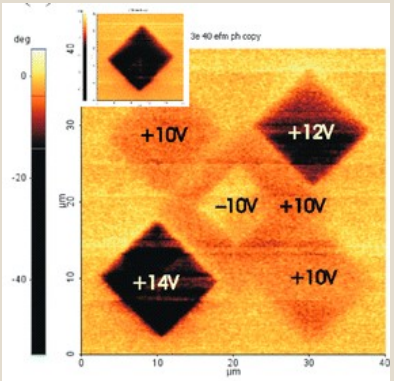


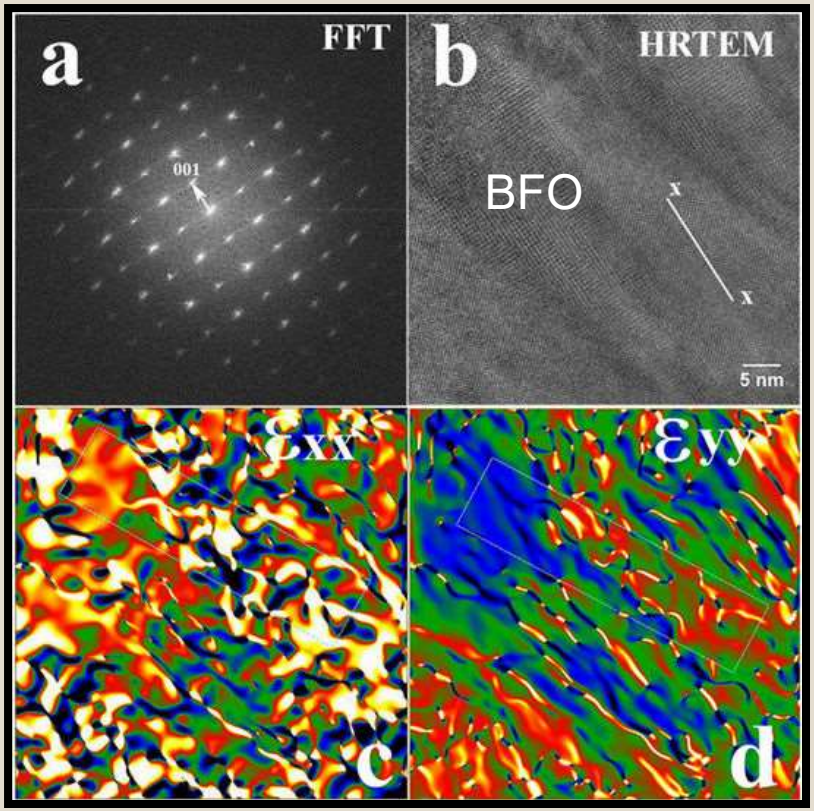


Ceria pyramidal nanostructures

- High permittivity materials $(1-x)Ba(Zr_{0.2}Ti_{0.8})O_3 - x(Ba_{0.7}Ca_{0.3})TiO_3$ (x=0.45)
- Multiferroic materials for photocatalitic and photovoltaic applications: $BiFeO_3$ thin films with high dielectric response

Out-of-plane PFM image for BCZT/STO thin films.

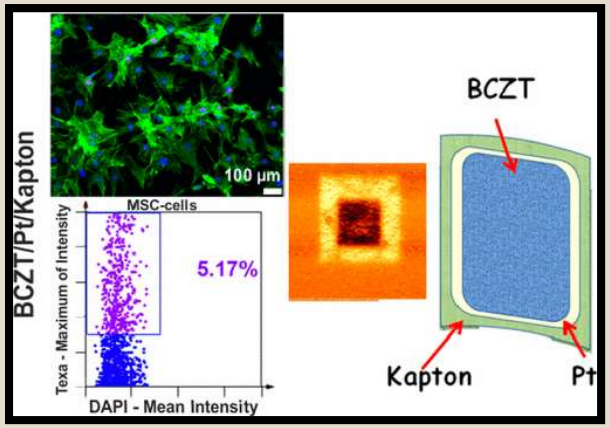


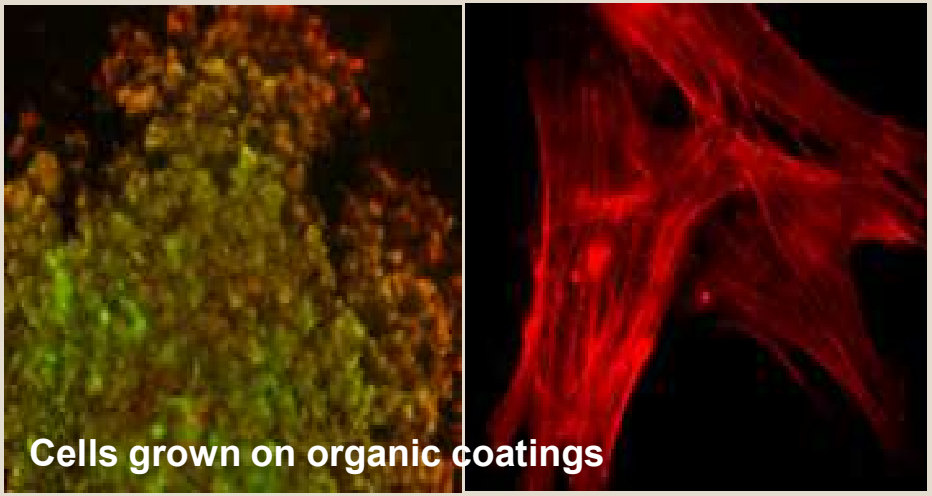


ENERGY

In the Lasers Department at INFLPR we are focused on creating new materials for sustainable sources of energy (generation and storage).

- Piezoelectric biocompatible materials: Lead-free piezoelectric (Ba, Ca)(Zr,Ti) thin films for biocompatible flexible devices
- Biomimetic coatings for tissue engineering applications



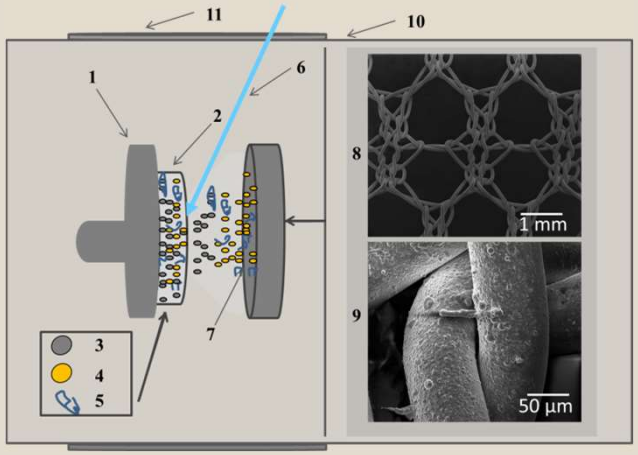


LASERS IN HEALTH AND BIOLOGY

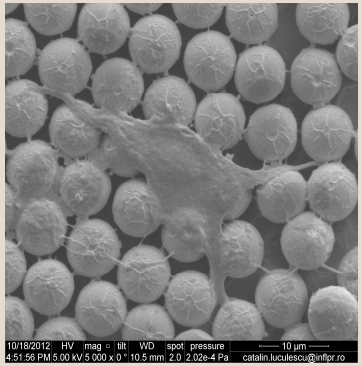
Researchers in the Lasers Department at INFLPR are undertaking basic research activities towards developing new methods for processing organic and biologic materials and finding new illness treatment methods.

LASERS IN HEALTH AND BIOLOGY

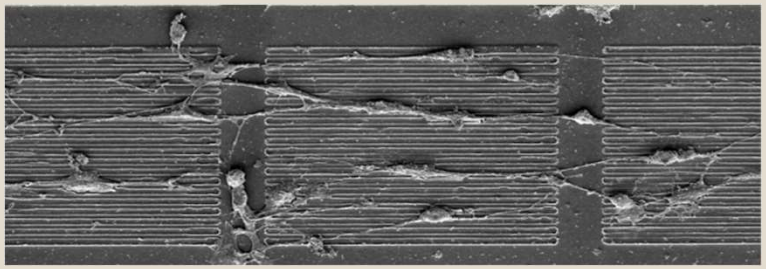
- Nano-coatings for hernia-repair meshes
- Bio-interface engineering using laser based methods
- Engineering micro and nano-scale topographies to control the cell-substrate interface
- Smart coatings-stimuli responsive



Hernia repair mesh coated by MAPLE with polymer:drugs



SEM images of fibroblast cell adhered onto PS microbeads pattern



SEM images of OLN cells polarized and aligned on line patterned chitosan coated surface

Laser induced Photochemistry (LLP)

TiO_2-based nanoparticles (10-40 nm)

- TiO_2 nanoparticles with majority anatase phase (reaching values of 97%) whose photocatalytic properties were tested, yielding 45% efficiency higher than the current industry standard Degussa P25

Fe based nanoparticles

- γFe_2O_3-based maghemite nanoparticles (<100 emu/g saturation magnetization,2-10 nm,Relative standard deviation~ 0.1)
- $Fe(C)@Fe_2O_3$ (oxide passivated iron nanoparticles) (<75 emu/g, 10-20 nm, core@shell feature)

- $Fe\text{-}Fe_xC$@polymer (polymeric passivated metallic + carbidic iron nanoparticles) (<60 emu/g, 10-30 nm, core@shell structure)

- $Fe\text{-}Fe_xC$@C (carbon encapsulated metallic-carbidic iron nanoparticles) with saturation magnetization up to 135 emu/g, 6.5-17 nm mean size, Relative standard deviation~0.1
- Fe nitrides, carbides, silicides or doped iron based NPs with: Co, C, Zn, Al, N, S, Si, I.

These iron -based nanocomposites were successfully tested as Contrast agent, in magnetically localized drug delivery with good cell penetration and hyperthermia effect, for magnetic separation,heat exchange nanofluid and conductometric gas sensors for reducing gases such as CO and CH_4 in presence of water vapors or for volatile organics such as ethanol

Sn based nanoparticles

- Sn metallic or Sn-Fe, Sn-Ge, Sn-Si, Sn-RGO or Sn-Ge-Si composite nanoparticles (mean size
- Sn@C and Sn-Fe-N@Polycarbosilazane core-shell nanoparticles
- SnO_x nanoparticles having different ratios between SnO_2 and SnO phases, also doped with cations Fe^{3+}, Al^{3+}, Zn^{2+} or anions such as F^-

These tin-based nanoparticles were tested as Li-storage component in anodes for Li-ion batteries, the most promising results were found for the smaller tin oxide nanoparticles.

Carbon-based nanoparticles

Carbon-based spheroidal nanoparticles with sizes under 50 nm and various structures: concentric-turbostratic, amorphous, fullerenic and with long stacked graphene bands concentrically (shell-shape structure) arranged or random interconnected which can be used as supports for noble metal nanocatalysts in fuell cells or for electroconductive composite films.

Carbon nanotubes (CNTs)

Multi wall CNT and nitrogen doped CNTs ranged from 2 to 65 nm by laser-induced chemical vapor deposition (LCVD)

Composites with nanoparticles

We employed our nanoparticles as fillers for various nanocomposites having organic polymers as matrices, such as carbon nanoparticles in epoxy resins, polyethylene, methylmethacrylate PMMA, poystyrene PS, silicone rubber etc in order to increase their electrical conductivity and/or thermal and mechanical properties. Methods using melted or dissolved polymers, as well as from monomers in liquid phase were used, including less used polymer infiltration. Solution-suspension polymerization method was used to obtain Fe@C - Polyaniline magnetic nanocom-posites by employing sodium carboxymethylcellulose CMCNa as hydrophylizing agent and $C_6H_5NH_3^+Cl^-$ as monomer. The same approach was successfully used to obtain various hydrogel composites by suspending our nanoparticles in aqueous solutions containing (meth)acrylates (monomers containing also reticulating agents) and initiators followed by thermally-initiated polymerization. A similar approach starting from aqueous suspensions of Fe@C nanoparticles stabilized with CMCNa was used to obtain magnetic nanocomposites having oxidic shells/matrices in the presence of liquid alcoxides such as tetraethoxysilane TEOS or tetrabuthoxytitanate TBOT.

Nanoparticle Suspensions

A very promising application area for our nanoparticle under the form of stabilized aqueous suspensions - known also as water-based nanofluids - is for thermal transfer as cooling or heating fluids without liquid phase change or with liquid boiling, as well as for solar thermal heating. We published papers regarding the use of nanomaghemite-suspended nanofluids in thermosiphons, and also concerning the properties of Fe_2O_3, SiC or Fe-C aqueous nanofluids. Other application is the use of magnetic nanoparticles-based fluids as magnetorheological fluids for dampers or lubricating agents

The magnetic nanoparticles - thus being abe to be directed and deparated using an external magnetic field - as suspensions in biological fluids have a wide range of applications from targeted drug delivery, labelling with fluorescent markers, contrast agents in techniques such magnetic resonance imaging MRI, tumor killing using alternative magnetic field-induced hyperthermia, photodynamic therapy, carriers of proteins, peptides, DNA, RNA to the capturing of toxins or valuable proteins from complex culture media (genetically modified cells, bacteria or yeasts secreting factors or proteins of medical interest).

PLASMA PROCESSING FOR CLEAN ENERGY PRODUCTION AND STORAGE

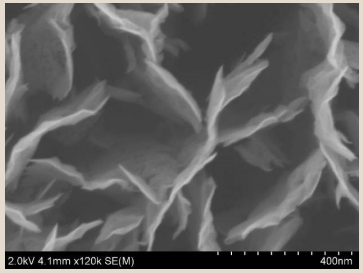
Clean eenvironment: Depollution and Biological decontamination by Plasma

- Cold atmospheric pressure non-thermal jets (plasma torch, DBD jets)
- Plasma in liquid technology
- Targeted substances: dyes, pesticides, pharmaceutical compounds.

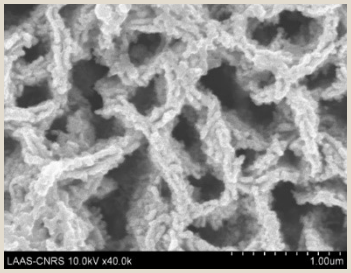
Clean Energy: nanomaterials for energy storage (batteries, supercapacitors) and plasma processing for fusion research

- Vertical graphene layers (Carbon NanoWalls CNW, nanofibers CNF);
- Nano and micro-particles (Tungsten) synthesis and treatments.
- Plasma cleaning of flat and complex shape surfaces.

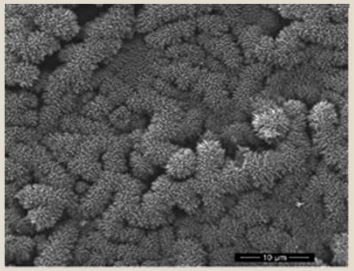
PLASMA PROCESSING FOR CLEAN ENERGY PRODUCTION AND STORAGE



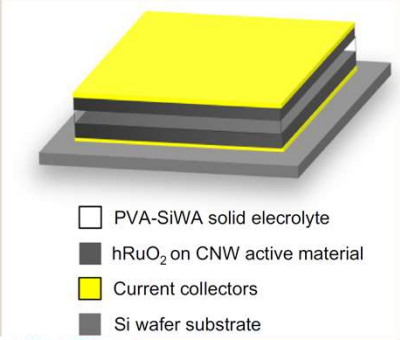
Carbon nanowalls: CNW



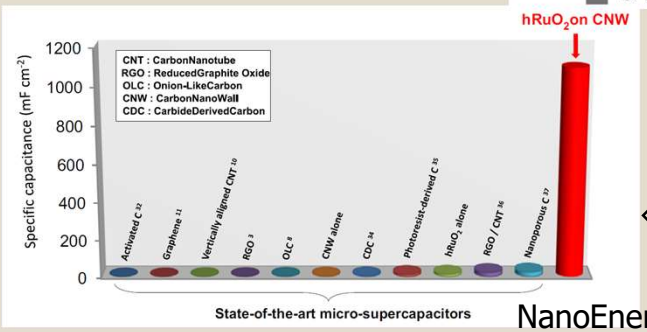
CNW coated with RuO_2



Hybrid: CNF over CNW



Supercapacitor structure



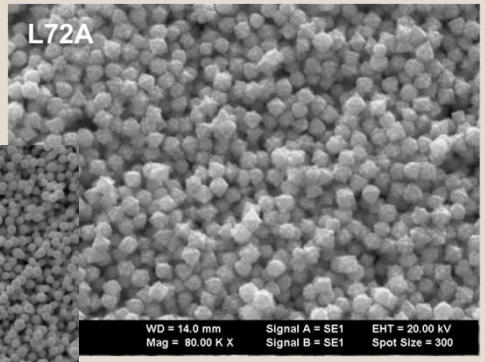
Electrode capacitance

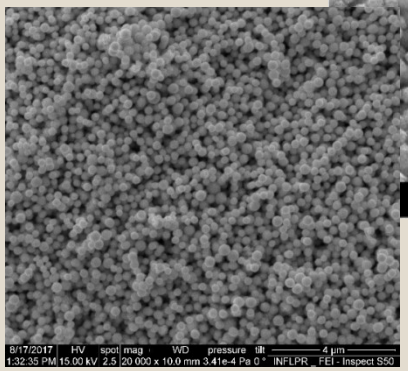
NanoEnergy, 2014(10) 2888-294

Nano, and microparticles (**W, Cu**..)

- Cluster source – by magnetron sputtering gas aggregation – MS GAS
- Atmospheric pressure plasma jets

W, nano: MS-GAS



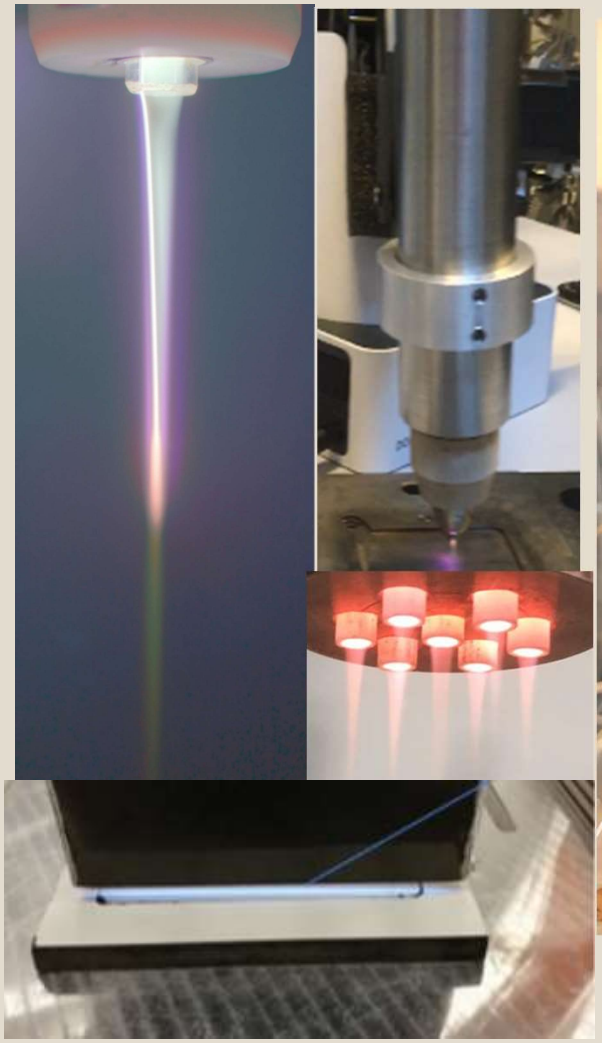


W, nano: microarc discharge

- W particles: Tritium retention
- WO3: Sensors, water splitting
- Np - platforms for study of cell growth

Nucl. Fusion 2019, 59, 086061
Nanomaterials, 2021, 11, 235

CLEAN ENVIRONMENT - PLASMA IN LIQUIDS



- Decomposition of hazardous substances and chemical contaminants in solution
  - Dyes: textile industry
  - Pesticides: Parathion, Reldan and Novadim

Cold atmospheric plasma jets: axial and planar

Plasma Chemistry and Plasma Processing 2020, 40, 1485–1505

THE TOOLS OF RESEARCH

Complete material and thin film characterization (morphology, structure, composition, optical, electric, etc.)

Systems for sensor testing

Thank you for your attention!

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